NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION

METHODOLOGY FOR THE FIELD EXTRACTION/PRESERVATION OF SOIL SAMPLES WITH METHANOL FOR VOLATILE ORGANIC COMPOUNDS FEBRUARY 1997

1.0 Scope and Application

1.1 This method describes the container preparation, field sampling and field extraction/preservatio procedure to be used in conjunction with the analysis of soil samples for volatile organics. The applicable analytical methods are SW-846 methods 8010B, 8015A, 8020A, 8021A, 8240B and 8260 found in the most recently promulgated edition of USEPA's Test Methods For Evaluating Solid Waste and the most current version of the Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program.

1.2 It is the laboratory's responsibility when analyzing samples obtained by this method to demonstrate internally that all NJDEP soil cleanup criteria for VOC's (last revised on 2/3/94, as contained in the April 1994 NJDEP Site Remediation News, Volume 6, Number 1, pages 13, 17-19) have been achieved. Should a laboratory know or suspect it has inadequate analytical sensitivity to meet any of the cleanup criteria, the laboratory shall not accept any samples unless the Department is notified in advance and the laboratory obtains approval.

2.0 Method Summary

2.1 Soil samples collected for volatile organic analysis must be handled in a manner which will minimize the loss of contaminants due to volatilization and biodegradation. Department experience and open literature indicate that, for the analysis of volatile organic compounds in soil, field extraction/preservation with methanol must be conducted to ensure that contaminants do not degrad or volatilize during sample handling and transport.

2.2 A small diameter soil core sampling device is used to collect a 10 gram (g) soil sample. The sample is extruded into a tared sample container, supplied by the laboratory performing the analysis, containing purge and trap grade methanol and surrogate compounds. The ratio of volume of methano to weight of soil is 2.5:1. A portion of the methanol extract is combined with organic free reagen water and analyzed by purge and trap GC or GC/MS.

3.0 Sample Containers

3.1 The recommended sample containers are a 60 ml (2 oz.) wide mouth packer bottle, a 60 straight sided wide mouth bottle and a 40 ml or 60 ml VOA vial. All sample containers should have a

open-top screw cap and a silicone rubber coated with Teflon [R] septa or other similar sample container. Some similar containers with Teflon[R] lined screw caps have shown to be susceptible to leakage. The type of container used should be tested to ensure leakage will not occur during shipment.

The use of larger volume containers will cause the layer of methanol over the sample to be minimized, making it difficult to extract an aliquot of methanol for analysis.

3.2 The standard 40ml or 60ml VOA vial can be used, but the small mouth may not accommodat some core samplers. The VOA vial is also unstable and susceptible to spillage.

4.0 Sample Container Preparation

4.1 Label each sample container with a unique numerical designation.

4.2 Fill the sample container with 25 mls of demonstrated analyte free purge and trap grad methanol.

4.3 An actual analysis should be traceable to the methanol used in the sample containers on the day the sample containers were prepared.

4.4 Record the lot number of the methanol used in the preparation of the sample containers. This information can be used for future reference in the event of suspected contamination of the methanol.

4.5 Employing a syringe, add the appropriate surrogate compounds to the methanol based on the analytical method. For methods 8010B, 8015A, 8020A, and 8021A, add each surrogate compound to the methanol yielding a concentration of approximately 1500 ug/l in each sample container. For methods 8240B, 8260A and the Medium Level Soil/Sediment Sample procedure of the Contract Laboratory Program Statement of Work, add each surrogate compound to the methanol yielding concentration of approximately 2500 ug/l in each sample container.

4.6 Immediately cap the container tightly and gently swirl.

4.7 Variations of the surrogate compounds may be used depending upon expected sample matrix interferences and contaminants.

4.8 Weigh each labeled sample container with the 25 mls of methanol and surrogate compounds to the nearest one tenth (0.1g) of a gram.

4.9 Record the weight in a bound logbook and on the chain of custody record with its corresponding numerical designation.

4.10 All sample containers must be supplied by the laboratory performing the analysis.

4.11 The prepared sample containers must be stored at 4 ^{o} $\pm$2^{o}C before shipment. The sample containers should be prepared no more than fourteen (14) days prior to shipment. It will be the responsibility of the laboratory to ensure the integrity of the sample containers remain contaminant free.

5.0 Sample Collection Methodology

5.1 Soil sample collection for volatile organic analysis must be performed with the use of a decontaminated small diameter coring device. A modified 10-30 ml disposable syringe or commercially available small diameter tube/plunger sampler is acceptable. The small diameter coring device must be capable of collecting the required amount of sample from larger diameter core samplers (split spoons, etc.) or from freshly exposed soils

5.2 Selection of the sample location for volatile organics must be based on the methods in the NJDEP Field Sampling Procedures Manual, May, 1992 and the site specific sampling plan.

5.3 If a modified disposable syringe is used it can be prepared in-house by cutting off the injection tip. Depending upon the construction of the syringe, small air vents must be cut into the plunger or the rubber tip and retaining post must be removed. These alterations to the plunger will prevent air fro being forced through or around the soil plug during subcoring and sample extrusion.

5.4 The small diameter core sampler must be capable of delivering the sample directly into the sample container. The outer diameter of the core sampler must be smaller than the inner diameter of the sample container to avoid loss of sample and ease the soil transfer process. **The sample from the small diameter core cannot be transferred to a secondary container such as another sample bottle, zip lock bag, aluminum foil, etc. prior to placement into the sample container with th methanol preservative.**

5.5 Use a small electronic balance or manual scale for measuring the weight of the soil in the syringe. The scale must be calibrated before use, and intermittently the calibration should be checked during the sampling day to ensure accuracy of the weight measurements.

5.6 Tare weigh the small diameter core sampler.

5.7 Once the sampling interval has been selected, trim off the surface soils of the sample interval to expose a fresh soil surface. The loss of volatile organics from the surface soils will occur if the soil has been exposed for a short period of time (during screening, etc.). The removal of the surface soils can be accomplished by scraping the soil surface using a decontaminated spatula or trowel. The sampling procedure must commence immediately once a fresh soil surface has been exposed.

5.8 Using a decontaminated coring device, collect 10g $\pm$2g (8-12grams) of sample (wet weight). Wipe the outside of the subcoring device to remove any adherent soil. The plunger of the coring device can be pulled back or completely removed allowing the open barrel of the subcore to be inserted into the soil. Depending upon the soil texture, depth or moisture content, the subcore can be inserted

straight into the soil, on an angle or multiple insertions can be performed to obtain the required sample weight.

5.9 Quickly weigh the sample while contained in the small diameter core sampler. Excess soil sample can be removed from the coring device by extruding a small portion of the core and cleaning away wit a decontaminated trowel or spatula. **If soil weight is below the weight limit, obtain additiona sample. Reweigh after each addition or removal of sample to the subcore until the target weight is attained (8-12g). Analytical results from a sample exceeding the weight maximums and minimums may be rejected and thus require resampling**.

5.10 When sampling soils consisting of similar textures and water content, sample weight can be estimated based on volume of previously weighed samples from sampling or practice core sampling to determine sample weights.

5.11 Immediately open the sample container and slowly extrude the soil core into the preweighed and prenumbered sample container supplied by the laboratory performing the analysis. Avoid splashing methanol out of the sample container. Do not insert the small diameter coring device into the mouth o small diameter sample containers (40ml or 60ml VOA vials) or immerse the small diameter soil coring device into the methanol.

5.12 Ensure the threads on the sample container and cap are free of soil particles. Use a clean brush or paper towel to remove the particles off the threads. The presence of soil particles compromises the seal of the container resulting in loss of methanol which may invalidate the sample.

5.13 Secure the lid of the sample container. Gently swirl the sample to mix and break up the so aggregate until soil is covered with methanol. **Do not shake.**

5.14 Do not attach any additional adhesive backed labels or tape to the sample containers. Record sample numbers on container avoiding covering laboratory identification number. Labels with wire or rubber band attachments may be used provided they can be removed easily for sample weighing. Record laboratory and field identification numbers on chain of custody and field notes.

5.15 The actual weight of soil will be determined by the laboratory performing the analysis.

5.16 Do not use or submit samples for analysis if any methanol has spilled from a sample container during shipment to the site or during sampling. Extra sample containers can be made available by the laboratory in case of accidental spillage of methanol in the field. The sample containers must be prepared in accordance with Section 4.0.

5.17 After sample collection, immediately return the containers to an iced cooler in an upright position. Sample containers can be placed in separate ziplock bags to protect other containers in cas of leakage during transport. The laboratory sample number or field sample identification number may be placed on the bag and crossed referenced on the Chain of Custody. Do not place additional adhesiv backed labels or tape on the sample containers. If any methanol is lost from a sample container upo arrival at the laboratory, the sample is invalid and resampling must be performed.

6.0 Moisture Determination

6.1 To report the sample results on a dry weight basis, collect one duplicate sample **not preserved with methanol** from each sample location for moisture determination. Tightly seal the container to prevent the loss of soil moisture. This sample does not require to be weighed or preserved wit methanol. A small volume sample container (15 mls or less) may be used for this sample to avoid possible sample shortages.

6.2 Weigh a 5-10g portion of the sample in a tared crucible.

6.3 Dry the sample overnight at 103-105 ^{o}C. Allow to cool in a desiccator before reweighing.

6.4 Determine percent dry weight by the following formula:

$$\% \text{ dry weight} \quad \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

6.5 Calculate sample concentration on a dry weight basis.

7.0 QA/QC Sample and Decontamination Requirement

7.1 Ambient Blank

7.1.1 An Ambient Blank is a QA/QC sample which will determine the potential contaminatio from ambient air during sampling procedures. This sample will provide a means to evaluate non-sample related contamination.

7.1.2 The Ambient Blank is prepared in the same manner as the sample containers described in Section 4.0. During sample collection, it is opened at the same time and next to the sample container and remains open during sample collection. It is closed at the same time as the sample container. It is performed at only one sample location in an area suspected of having the highest ambient contamination.

7.1.3 **The collection of an Ambient Blank is not required when sampling is performed using the methanol extraction/preservation techniqu** . It will be optional at the discretion of the site investigation team, or will be required on a site specific basis if previous elevated analytical result are suspected due to contamination from the sampling environment.

7.1.4 If Ambient Blanks are employed, the frequency of collection should be one (1) per day or at the discretion of the investigation team based on site conditions.

7.1.5 Results of the Ambient Blank must be reported as a solid sample where a sample weight of 10g and 100% dry weight is assumed.

7.2 Field Blank

7.2.1 A Field Blank is a QA/QC sample which will determine potential contamination fro sampling equipment used to collect and transfer samples from the point of collection to the sample container.

7.2.2 A Field Blank is performed by pouring demonstrated analyte fr **water** from one sample container, over each piece of sampling equipment required for sample collection and into a separate set of identical sample containers. Additional information on Field Blanks can be found in the NJDEP Field Sampling Procedures Manual, May 1992.

7.2.3 **A Field Blank is not required when sampling with the methano extraction/preservation technique.** It is optional, or will be required on a site specific basis i previous elevated analytical results are suspected due to cross contamination from sampling equipment.

7.3 Trip Blank

7.3.1 A Trip Blank is a QA/QC samp le which will determine additional sources o contamination that may potentially influence the samples. The sources of the contamination may be from the lab, sample bottles or during shipment.

7.3.2 A Trip Blank is prepared at the same time and in the same manner as the sample containers as described in Section 4.0. The Trip Blank must accompany the sample containers to the field and back to the laboratory along with the collected samples for analysis. It must remain sealed at all times until it is analyzed at the laboratory.

7.3.3 **A Trip Blank is required when sampling with the methanol extraction/preservation technique.** It will be required due to potential cross contamination from sample shipment or fro handling at the laboratory.

7.3.4 The frequency of collection for the Trip Blank must be at a rate of one (1) per sample shipment.

7.3.5 Results of the Trip Blank must be reported as a solid sample where a sample weight of 10g and 100% dry weight is assumed.

7.4 Duplicate Samples

7.4.1 P rform duplicate samples at a rate of five (5) percent (1 per 20 samples).

7.4.2 Duplicate samples must be obtained from the same location and soil type to minimize location as a potential source of variation in the analytical results. Separate core samples should be obtained for the sample and duplicate sample.

7.5 Sample and Sample Container Handling Time

7.5.1 Sample handling time is to control the length of time bottles are shipped to the site and held on site. The standard four (4) day handling time for sample containers and samples remains the same. Obtain additional information on handling times from Chapter 2 in the NJDEP Field Sampling Procedures Manual, May 1992.

7.5.2 As stated in N.J.A.C. 7:26E-2.1(a)15, samples must be delivered to the laboratory no later than 48 hours after sample collection.

7.6 Decontamination of Sampling Equipment

7.6.1 All equipment used for sampling must be decontaminated prior to use.

7.6.2 Decontamination of sampling equipment must follow the procedures in the NJDEP Field Sampling Procedures Manual, May 1992 for soil sampling equipment. If modified disposable syringes are utilized, they should be discarded if the three step cleaning procedure will not remove the contamination since exposure to acetone may damage the sampling tool.

7.7 General Quality Assurance

7.7.1 Quality assurance requirements have been established to maintain sample integrity. Their primary objectives are to maintain the physical form and chemical composition of the sample and to prevent contamination from other sources or cause changes in contaminant concentrations. Chapter 2 in the NJDEP Field Sampling Procedures Manual, May 1992 may be consulted for further details on other sampling QA/QC criteria and procedures.

8.0 Field Analysis

8.1 Field analytical methods may be employed during an investigation to aid in the selection or elimination of samples for laboratory analysis. When collecting samples for field analysis, collect duplicate sample for laboratory analysis. This prevents returning to a sample location and resampling at a later time. Any methanol preserved samples not submitted for laboratory analysis are a hazardou waste and must be disposed of on-site or by the laboratory according to State and Federal regulations. To avoid this problem, the following procedure can be used:

8.1.1 Using the sampling method in section 5.0, use an EnCor [R] core sampler to obtain a duplicate sample for laboratory analysis. Store the soil for laboratory analysis in the core sampler by sealing the end(s) of the core with the end caps supplied with the EnCor [R] sampler. **Eliminate headspace in the sampler.**

8.1.2 Label the core for lab analysis and immediately cool the sample. The core sample may be stored at 4°C on ice for a maximum of six (6) hours prior to preserving with methanol. This intermediate storage method can only be used if samples are field analyzed.

8.1.3 Perform the selected field analytical procedure on the duplicate sample and document the field analysis in accordance with the NJDEP Field Analysis Manual, July 1994.

8.1.4 If soil from a sample location is selected for laboratory analysis, preserve the iced cor sample with methanol. Samples must be preserved with methanol within the six (6) hour field holding time.

8.1.5 **Use this procedure only when performing field analysis of the samples (i.e. Field GC, Immunoassay, etc.).**

9.0 Laboratory Analysis

9.1 Upon arrival of the sample at the laboratory, weigh the sample container to the nearest one tent (0.1g) of a gram to determine the weight of soil placed in the sample container.

9.2 Subtract the weight of the container, methanol and surrogates from the total weight of the sample container with the soil sample. This gives the wet weight of the soil sample.

9.3 Proceed with the analysis of the sample using the "high concentration" methodology of the requested SW-846 analytical method or the "Medium Level Soil/Sediment Samples" procedure of the USEPA Contract Laboratory Program Statement of Work. In both instances, start the analytical procedure at the point where approximately 1ml of methanol extract is to be transferred to storage.

9.4 Using the non-methanol preserved duplicate sample, determine the dry weight of the sample.

10.0 Shipping Procedures

10.1 Methanol is considered a hazardous material therefore shipping of the sample containers is regulated by the U.S. Department of Transportation and the International Air Transport Association (IATA). The rules of shipment set in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179) and the current edition of the IATA Dangerous Goods Regulation must be followed when shipping methanol between the laboratory and the field. Consult the above documents or the shipping company for additional information.

10.2 The shipment of the quantity of methanol used for the sample preservation falls under the exemption for small quantities. A summary of the requirements for shipping samples follows. Refer to the code for a complete review of the requirements.

10.2.1 The maximum volume of methanol in a sample container is limited to thirty (30) mls.

10.2.2 The sample container must not be full of methanol.

10.2.3 The sample container must be stored upright and have the lid held securely in place. The mechanism used to hold the cap in place must be able to be completely removed so weight is not added to the sample container.

10.2.4 Sample containers must be packed in a sorbent material capable of absorbing spills fro leaks or breakage of the sample containers.

10.2.5 The maximum sample shuttle weight must not exceed 64 pounds.

10.2.6 The maximum volume of methanol per shipping container is 500mls.

10.2.7 The shipper must mark the sample shuttle in accordance with shipping dangerou goods in acceptable quantities.

10.2.8 The package must not be opened or altered until no longer in commerce.

11.0 Safety

11.1 Methanol is a toxic and flammable liquid. Therefore, methanol must be handled with all safet precautions related to toxic and flammable liquids. Inhalation of methanol vapors must be avoided. Vials should be opened and closed quickly during the sample preservation procedure. Methanol must be handled in a ventilated area. Use protective gloves when handling the methanol vials. Store methanol away from sources of ignition such as extreme heat or open flames. The vials of methanol should always be stored in a cooler with ice at all times.

12.0 References

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